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Atomic structure, electronic and optical properties of Si nanocrystals embedded in β-cristobalite and α-quartz

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We use DFT calculations to study the atomic structures, the optical and electronic properties of silicon nanocrystals (nc-Si) embedded in β-cristobalite and in α-quartz matrix. We show that the optical properties are influenced by the matrix type. The energy range of the absorption spectrum of nc-Si in α-quartz matrix is more extended than that of nc-Si in β-cristobalite. The presence of Si-O-Si bridge bonds at the nc-Si/β-cristobalite interface favours the stability of the system. The energy gap of nc-Si with interface defects is larger than that of nc-Si without interface defects.

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I. INTRODUCTION

The use of silicon in optical applications has long been limited by the small and indirect band gap until visible photoluminescence (PL) has been discovered in porous Si two decades ago [1]. After that, the intense visible PL with respect to porous silicon in the the system of Si nanocrystal embedded in SiO_2 matrix (nc-Si/SiO_2) has been noticed [2]. It is now commonly admitted that the peculiar photoluminescence properties of nc-Si are due to the quantum confinement of the generated photocarriers within the nc-Si as well as to specific electronic states localized at the nc-Si/SiO_2 interface [3–5]. Since then, materials composed of silicon nanocrystals embedded in SiO_2 matrix have been produced by various techniques. Si nanocrystals were formed by Si ion implantation into SiO_2 matrix [6, 7], nc-Si embedded in an amorphous SiO_2 matrix is prepared by reactive pulsed laser deposition combined with a postannealing treatment [8]. In these papers, authors have shown that Si^0 is associated to nc-Si, Si^{4+} corresponds to SiO_2 while the nc-Si/SiO_2 interface region contains Si^{n+} oxidation states where n=1-3. This may lead to two kinds of interface defects: the Si=O double bond and the Si-O-Si bridge bond where one oxygen atom relates two silicon atoms of nc-Si.

The simulation of a nc-Si embedded in the SiO_2 matrix requires to deal with hundreds atoms since the experimental nc-Si diameter is in the 5-30 Å range. The huge number of atoms is the main reason why the theoretical works on nanocrystals are principally based on tight binding calculations [9], potential approaches [10, 11] and calculations using the Density Functional Theory (DFT) on hydrogen passivated Si nanocrystals [12–15]. Thus, there are still only a few DFT calculations [16, 17] on embedded and realistic nanocrystals. Daldosso *et al.* [16] were the first to propose a DFT geometry of a small nanocrystal of 10 Si atoms embedded in β-cristobalite. However, the study of defects on the surface was not proposed. Structural properties of large nanocrystals (around 30 Å) were investigated with Monte Carlo simulation using force field model [10]. In such approach, no Si=O bond can be formed at the nc-Si surface and the authors concluded that the low-energy geometries of the nc-Si/SiO_2 interface contain Si-O-Si bridge bonds. Moreover, the fraction of bridge bonds sharply decreases from 62% to 33% when the nc-Si size decreases from 35 to 10 Å.

In the present paper, we realize the theoretical simulations of nc-Si embedded in different crystalline silica matrix and propose to study the influence of the matrix as well as the interface defects on the optical and electronic properties. Section 2 deals with the computational method. In section 3, we present three models of nc-Si embedded in α-quartz and in β-cristobalite with and without interface defects in order to describe the influence of these parameters on the electronic and optical properties of nc-Si in a silica matrix. Here, we choose the β-cristobalite because it is the form closer to the crystalline silicon structure and this ensures one of the simplest Si/SiO_2 interface. The α-quartz is chosen because it is the most stable silica crystalline form. The results of atomic, electronic and optical properties of nc-Si/SiO_2 will be presented in section 4, 5 and 6.

II. COMPUTATIONAL METHOD

We have used Density Functional Theory under the Local Density Approximation as implemented AIMPRO package [18, 19] with Gaussian basis sets and pseudopotentials developed by Hartwigsen *et al.* [20]. Each of the 2s and the three 2p valence orbitals of Si and O atoms has been described by the use two contractions of four gaussians. Besides, a d-Gaussian type polarization function is added for each atom. The exponents and coefficients of this basis set are optimized in α-quartz SiO_2. Using this basis, β-cristobalite lattice parameter has been correctly evaluated to 7.35 Å which is 2.6% larger than the experimental value. Brillouin zone sampling is integrated using the scheme MP proposed by Monkhorst-Pack [21]. We check the energy convergence as a function of the number of k points in order to choose an optimal k point grid for each system. We realize the total relaxation (atomic positions and lattice parameters). The electronic energy loss spectroscopy (EELS) is simulated by calculating -Im$(\epsilon(E)^{-1})$ where ϵ is the dielectric function and E is the energy loss [22]. The EELS spectra are broadened using a Lorentzian function. The formation energy of a nc-Si in SiO_2 informs on the stability of each simulated structures. Since these structures contain only neutral defects, the formation energy can be evaluated as described by Eberlein et al. [23]: $E_f = E_{tot} - n_{Si}\mu_{Si} - n_O\mu_O$

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where E_{tot} is the total energy of the supercell containing n_{Si} silicon atoms and n_O oxygen atoms. μ_{Si}, μ_O are the chemical potentials of Si and O. The chemical potentials satisfy the condition that $\mu_{Si}+2\mu_O$ is equal to the energy of a SiO_2 group in β-cristobalite. Silicon nanocrystals are produced from substoichiometric SiO_x films containing excess silicon atoms [16] so that nc-Si/SiO_2 can be considered as a Si-rich system. The chemical potentials are then : $\mu_{Si} = \mu_{Si}^{bulk}$ and $2\mu_O = \mu_{O2} - H_f$, where μ_{Si}^{bulk} is the energy of a Si atom in bulk silicon, μ_{O2} is the oxygen molecule energy in triplet state, the calculated heat of formation H_f is the difference between the energies of one Si and two O atoms in their standard states and the energy of a SiO_2 group in β-cristobalite.

On the clusters built from the structures found by LDA calculations on nanocrystals embedded in SiO_2, we performed molecular calculations with CRYSTAL06 code [24]. Within the B3LYP approximation, the HOMO/LUMO (Highest Occupied Kohn-Sham Orbital/Lowest Unoccupied Kohn-Sham Orbital) energy differences were evaluated using the basis sets denoted 66-21G* [25], 6-31G* [26] and 31G* [26] for the silicon, oxygen and hydrogen atoms respectively.

III. SI NANOCRYSTAL STRUCTURES

We build different nc-Si/SiO_2 structures in order to test the influence of the presence of defects at the nc-Si/matrix interface and of the nature of matrix on the electronic properties of the nc-Si.

A. nc-Si_{35} in β-cristobalite

We create the nc-Si embedded in β-cristobalite (Fd3m cubic phase of SiO_2). A single β SiO_2 cubic cell contains eight SiO_2 units. The β-cristobalite has a diamondlike symmetry with an oxygen atom in the centre of two silicon atoms so that the Si-O-Si bond angle is equal to 180°. The experimental lattice constant is 7.16 Å. To model a Si nanocrystal, we design a 3x3x3 β-cristobalite SiO_2 supercell. We then remove 52 O atoms from the centre in order to buid a silicon rich region containing 35 silicon atoms (called nc-Si). The resulting supercell comprises 216 Si atoms and 380 O atoms.

B. nc-$Si_{35}O_{12}$ in β-cristobalite

Nc-Si embedded in SiO_2 matrix with Si-O-Si bridge bonds at interface have been obtained by Monte Carlo simulations [10]. The percentage of bridge bonds reduces to 30% in the 10 Å nc-Si. Thus, we create a nc-Si containing 35 Si atoms and 12 Si-O-Si bridge bonds corresponding to 30% of interface bonds. We design a 3x3x3 β-cristobalite supercell. We remove 40 oxygen atoms from the supercell centre leading to a silicon rich region containing 35 silicon atoms (the so-called nc-Si) and 12 oxygen atoms surrounded by the β-cristobalite matrix. The nc-Si diameter is the same as the nc-Si_{35} but the nc-Si/SiO_2 interface contains twelve Si-O-Si bridge bonds.

C. nc-Si_{17} in α-quartz

The SiO_2 α-quartz has a hexagonal structure with a primitive unit cell containing three SiO_2 units. To model a nc-Si embedded in α-quartz we design an orthogonal supercell of α-quartz whose dimensions are equal to 14.4 Å, 16.7 Å and 16 Å. We remove 16 oxygen atoms from the supercell centre to form a Si-rich region which contains 17 Si atoms. The resulting supercell contains 108 silicon atoms and 200 oxygen atoms. The nc-Si/SiO_2 interface has no Si-O-Si bridge bond.

D. Isolated Si clusters

From the relaxed atomic structures of nc-Si_{35} and nc-$Si_{35}O_{12}$ systems, we extract all Si atoms of the nanocrystals and their first neighbour O atoms. The clusters are produced by adding hydrogen atoms so that the Si-O-H angle is equal to the corresponding Si-O-Si angle at the nc-Si/SiO_2 interface and by setting the O-H distance to 1 Å. By this approach we obtain two Si clusters: $Si_{35}(OH)_{36}$ and $Si_{35}O_{48}H_{36}$.

IV. RESULTS AND DISCUSSION

A. Atomic structure of nc-Si

Nanocrystals in β-cristobalite (refered to nc-Si_{35} and nc-$Si_{35}O_{12}$): The supercells containing the nc-Si_{35} nanocrystal and the nc-$Si_{35}O_{12}$ are totally relaxed [fig. 1]. In both cases, the nanocrystal diameter is equal to 11 Å. The final average Si-Si bond length within the nc-Si in these two models is about 2.4 Å (+6% with respect to the value optimized for crystalline silicon). The equilibrium supercell parameter is reduced about 8% with respect to the theoretical parameter optimized for a supercell of pure β-cristobalite SiO_2.

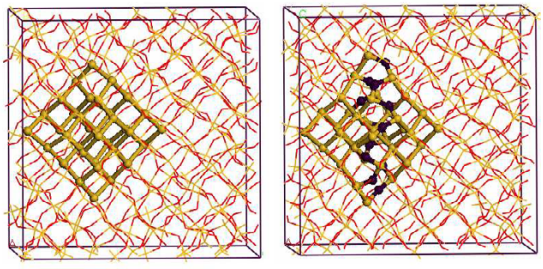

FIG. 1: Final structure of nc-Si_{35} (left) and nc-$Si_{35}O_{12}$ (right). The silicon atoms of the nanocrystals are yellow, the interface oxygen atoms are dark violet

In a region which extends over 3 Å from the nanocrystal surface, the Si-O distances between Si atoms of nc-Si and interface O atoms are distributed from 1.63 Å to 1.66 Å and the Si-O-Si angles are distributed from 158° to 175°. It is the interface region. Outside the interface region, the Si-O distances are smaller (between 1.6 Å and 1.61 Å) and the Si-O-Si angles become smaller (between

136° and 149°). These distances and angles are very similar to those in amorphous SiO_2 [4]. Thus we can evaluate the interface thickness to 3 Å. This value is similar to the result of DFT calculations on a plane Si/SiO_2 interface proposed by Neaton et al. [27].

nc-Si_{17} in α-quartz: after the total relaxation, we obtain the final structure of the nanocrystal in α-quartz [fig. 2]. The cell sides are reduced of 1% with respect to the initial values. As in the α-quartz matrix, the atomic density is higher than in β-cristobalite matrix, these cell sides are less compressed than in β-cristobalite systems. The nc-Si is within a sphere of 8 Å diameter, the nanocrystal contains 17 Si atoms among which 5 Si^0 and 12 Si^{3+}. The average Si-Si bond length between the first neighbours of nc-Si is about 2.6 Å, +14% with respect to the value optimized for crystalline silicon. The average Si-Si-Si bond angle of the five tetrahedrons [fig. 2] is equal to 103°, -5% with respect to the value in bulk silicon.

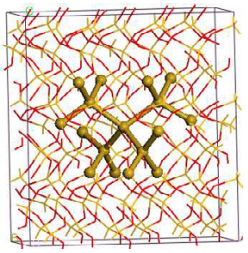

FIG. 2: Final structure of nc-Si_{17} in α-quartz

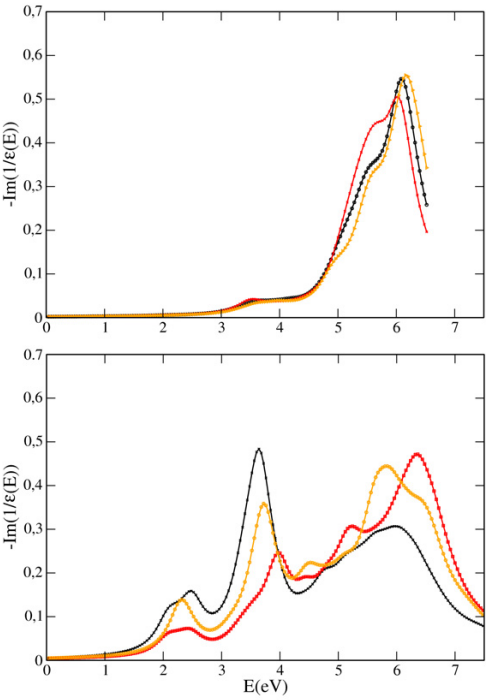

FIG. 3: Absorption spectrum of the nc-Si_{10} in β-cristobalite (top) and of the nc-Si_{17} in α-quartz (bottom)

B. Influence of the matrix

The nc-Si_{17} in α-quartz can be considered as the suboxide SiO_x system where $x = 1.85$. In our previous paper [28] we presented the study of the nanocrystal concerning 10 silicon atoms (nc-Si_{10}) in β-cristobalite. This system contains 64 silicon atoms and 116 oxygen atoms. The nc-Si_{10} in β-cristobalite is considered as the SiO_x system with $x = 1.81$. We use the results of the nc-Si_{10} in β-cristobalite and of the nc-Si_{17} in α-quartz to discuss the influence on the absorption of these two silica matrix at similar x.

The absorption spectra -Im$(\epsilon(E)^{-1})$ of the nc-Si_{10} in β-cristobalite and of the nc-Si_{17} in α-quartz are plotted in figure 3. The three curves corresponding to the diagonal values ϵ_x, ϵ_y and ϵ_z of the dielectric constant matrix. The absorption band of nc-Si_{10} in β-cristobalite lies in the 3-7 eV range while that of nc-Si_{17} in α-quartz is more extended (1.5-7 eV range). These energy bands are comparable with the experimental results [29, 30]. In the spectrum of nc-Si_{10} in β-cristobalite, only one intense peak is observed at about 6 eV. In the spectrum of the nc-Si_{17} in α-quartz, the peak at about 2.2 eV corresponds to the HOMO-LUMO transition. A more intense peak is seen at 3.5 eV corresponding to the HOMO-LUMO+2 transition where LUMO+2 is the second unoccupied Kohn-Sham orbital over the LUMO. The presence probabilities of these two levels are presented in figure 4. The distributions of these two levels are localized within the nanocrystal, around the atom Si^0 in the nanocrystal centre. A comparison of these two spectra leads to the conclusion that the surrounding matrix influences strongly the absorption behaviour of nc-Si.

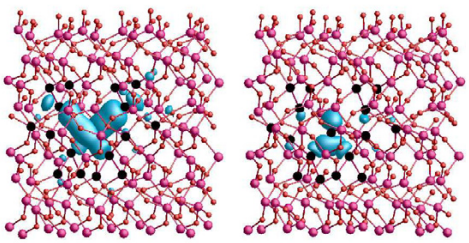

FIG. 4: Charge density isosurfaces of the HOMO (left) and of the LUMO+2 (right) of nc-Si_{17}, the silicon atoms of the nanocrystal are black, the silicon atoms in the matrix are the red and big balls, the oxygen atoms are the red and small balls

C. Role of interface defects in electronic property of nc-Si in β-cristobalite

The nc-$Si_{35}O_{12}$ contains 12 Si-O-Si bridge bonds at the interface, corresponding to a fraction of 30% of interface

bonds. In the structure of nc-Si embedded in an amorphous SiO_2 simulated by Monte Carlo approach [10], the fraction of bridge bonds in the 10 Å nanocrystal is equal to 33%. The formation energies of nc-Si_{35} and nc-$Si_{35}O_{12}$ are respectively equal to 33 eV and 25 eV. Hence, the nc-$Si_{35}O_{12}$ with bridge bonds at the interface is the more stable structure. We can conclude that the presence of Si-O-Si bridge bonds with a fraction of 30% of interface bonds at the nc-Si surface favours the stability of the system of nc-Si embedded in a silica matrix.

The electronic properties of these two nc-Si are characterized by their interface defects. The LDA band gap of the nc-$Si_{35}O_{12}$ is larger than that of the nc-Si_{35}. By creating the Si-O-Si bridge bonds at the interface, we increase the energy gap of nanocrystal. The same result has been obtained for nc-$Si_{10}O$ and nc-Si_{10} [28]. In the nc-Si_{10} there is no Si-O-Si bond at the interface while the surface of nc-$Si_{10}O$ contains a Si-O-Si bridge bond. We conclude that the energy gap seems to increase with the number of the Si-O-Si bridge bonds at the nc-Si/SiO_2 interface.

The description of the band gap is efficiently improved by the use of the B3LYP approximation [31], which is implemented in CRYSTAL06 code [24]. On the basis of the AIMPRO relaxed supercells, we have thus extracted clusters (see III D). In the case of $Si_{35}(OH)_{36}$ and $Si_{35}O_{48}H_{36}$ clusters, the LDA HOMO/LUMO energy differences are very close to the values obtained on supercell calculations. It seems sufficient to take into account only the first neighbour oxygen atoms in the case of a cluster calculation to reproduce the supercell calculations and to propose a realistic model. For the cluster without interface defect ($Si_{35}(OH)_{36}$), the B3LYP gap is equal to 3.1 eV while that of the cluster with Si-O-Si bridge bonds ($Si_{35}O_{48}H_{36}$) is equal to 3.6 eV. Our results are in accordance with the optical energy gap mesured by absorption spectroscopy. Kim *et al.* [32] have obtained optical gaps of 3.04 eV, 2.61 eV and 2.12 eV for nc-Si whose diameters are respectively equal to 10, 22 and 30 Å.

The electronic presence probabilities of the nc-Si_{35} and the nc-$Si_{35}O_{12}$ have been calculated. The electron presence probabilities of the HOMO in these two systems are mainly localized on the Si atoms of nc-Si and a weaker presence probability is observed on the O atoms at the nc-Si/SiO_2 interface. The orbital localization on the nc-Si region supports the view of nearband-edge states related to nc-Si, while the contribution on the O atoms indicates the role of the nc-Si/SiO_2 interface.

We draw the conclusion that the nc-Si/SiO_2 interface can participate directly to the optical activity of the system. The presence probabilities of the LUMO level of these two systems tend to be localized mainly on the Si atoms inside the nanocrystals [fig. 5]. Thus, the part of the presence probability at the nc-Si/SiO_2 interface is higher in the case of nc-$Si_{35}O_{12}$ system than in the nc-Si_{35} system. Hence, the presence of interface defects seems to increase the probability of formation of electron-hole pairs at the surface of nanocrystals.

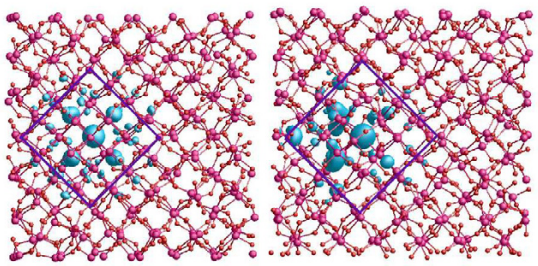

FIG. 5: Charge density isosurfaces of the LUMO of nc-Si_{35} (left) and of nc-$Si_{35}O_{12}$ (right). The violet squares limit the surfaces of the nanocrystals

V. CONCLUSION

We have used first-principles calculations to study the atomic, optical and electronic properties of silicon nanocrystals (nc-Si) within an insulating matrix (SiO_2).The crystalline phase of the matrix (α-quartz or β-cristobalte) and the presence of defects at the nc-Si/SiO_2 interface (Si-O-Si bridge bonds) influence the electronic properties as well as the structure stability. The presence of Si-O-Si bridge bonds at the nc-Si/β-cristobalite interface favors the systems stability. The absorption band of nc-Si is more extended in α-quartz matrix [1.5 eV - 7 eV] than in β-cristobalite matrix [3 eV - 7 eV]. It means that nc-Si embedded in α-quartz can be excited by a wider range of photon energies. Finally, such interface defects increase the band gap, which is usefull in the field of silicon based photonics using visible light devices.

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